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Explosive Chemical Signatures from Military Ordnance

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Prepared by
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Abstract

Military testing and training ranges contain large numbers of unexploded ordnance and range scrap. The significant safety issues with unexploded ordnance require very costly and time consuming efforts to locate and distinguish explosive containing items from harmless ordnance fragments, target practice units and other range scrap. This work was completed to measure the explosive chemical signature emitted from a small set of unexploded ordnance items to determine if chemical sensing could be a viable discrimination method. The work included measurement of ordnance surface residues and flux into water during immersion tests both prior to and after conventional firing and field recovery. Measurement of chemical residues in soil samples collected adjacent to unexploded ordnance items were performed to determine the net chemical signature derived from the emitted flux and biochemical degradation at two ranges with distinctly disparate environmental conditions. The data collected in this effort indicates that a unique persistent distinguishing trace chemical signature emitted from unexploded ordnance does not prevail under all test and field conditions sampled. This indicates that trace chemical sensing for unexploded ordnance discrimination may not be a robust technique in support of military range cleanup efforts.

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1.0 Introduction

Sensing the explosive chemical signature as a method to discriminate live (containing high explosive – HE) from inert (target practice – TP) unexploded ordnance (UXO) has been considered due to the advances in sensitivity and specificity of advanced chemical sensing technologies. The success of this approach is dependent on the rate of release of the chemical signature of the main charge explosive being greater than the loss rate in the environment. This effort was completed to:

- Assess the nature of the release rate of explosive chemical signatures from military ordnance, and
- Measure field soil residues adjacent to ordnance found on range sites with differing environmental conditions.

Moving actual UXO identified on a range to testing facilities would be problematic due to safety concerns with handling fused UXO. Therefore a testing program was devised that would use actual ordnance where the primary explosives in the fuses were removed. The ordnance would be fired using normal procedures on-site at Sandia, recovered, and moved to an on-site lab for testing. In this way the ordnance would experience similar impact effects, but could be safely recovered for leakage testing.

Work scope was organized into the following subtasks:

- Ordnance Acquisition
- Pre-Shot Surface Residue
- Pre-Shot Immersion Tests
- Ordnance Firing
- Post-Shot Surface Residue
- Post-Shot Immersion Tests
- Field Residues

Ordnance acquisition through Rock Island Arsenal began in Fall 1998. While Sandia National Laboratories had previously acquired ordnance from this source, new protocols required execution of a revised interagency transfer agreement between the U.S. Department of Energy and the U.S. Department of Defense. This was completed in late CY 1998. Early in CY1999 the Kosovo conflict placed our acquisition on lower priority. These events caused delayed delivery and initiation of this effort until we received the ordnance in July 1999. Table 1 shows the type and quantity of the units received.

Table 1. Ordnance Received

Ordnance Type	Quantity
60 mm mortar – Target Practice with black powder spotting charge	12
60 mm mortar – HE M49A4 with PD fuze for M2 and M19 mortar. Comp B. Loaded 7-75.	12
81 mm mortar – Target Practice with black powder spotting charge	12
81 mm mortar – HE M43A1 with PD fuze. TNT. Loaded 7-53.	12
105 mm artillery – Target Practice	12
105 mm artillery – M760 Dualgram w/ supplemental charge for howitzer M119 only. TNT. Load date unknown.	12

2.0 Pre-Firing Chemical Signatures

2.1 Removable Surface Contamination

The amount of chemical residue on the exterior surface of the ordnance items will directly influence the initial release of chemical into the environment. Measurement of the surface residues was performed using two methods.

- Surface residues were transferred to filter paper soaked with methanol (swipe samples), and
- Paint was scraped from ordnance items.

Chemical leakage over long time periods would be derived from the main charge, passing through assembly seams or damaged locations on UXO. Long term leakage was measured with aqueous immersion tests, using repetitive time sequenced samples.

2.1.1 Materials and Methods

Surface Swipe Tests

Ordnance items were removed from the crates and cardboard packaging tubes at the Sandia ordnance receiving area. Whatman #1 filter papers (2.5 cm diameter) were soaked with methanol from a squirt bottle and held until dripping ceased. The filter paper was placed onto the ordnance item and left until evaporation of the methanol was visibly complete. Methanol was chosen as a solvent because the explosive chemicals have good solubility, but the methanol will not dissolve the paint matrix. All twelve of the HE filled ordnance items were sampled. Three each of the TP ordnance were sampled. For the 60 mm and 81 mm mortars, six (6) each filter paper samples were collected from each mortar. All six samples were placed as a composite into a 5 dram amber vial. For the 105 mm artillery, twelve (12) each filter paper samples were used. The top six (6) and bottom six (6) samples were placed in separate vials as composites. Figures 1, 2, and 3 show the swipe samples in place on the 81 mm mortars, 60 mm mortars and 105 mm artillery, respectively.

At the lab, 3 mL of acetonitrile was placed into each vial, completely immersing the composite filter paper samples. Each was shaken by hand and left at room temperature for about 1 hour. Aliquots were removed by disposable pipette and placed into autosampler vials. Quantitation was performed with a 1 uL injection into a HP 6890 Gas Chromatograph equipped with a micro electron capture detector and a RTX 225 0.53mm x 6 m 0.1 µm film thickness column. The split/splitless injector was programmed for a 220°C inlet temperature, starting column temperature of 100°C for 2 minutes, ramped to 200°C at 10°C/min, then held for 7 minutes. Table 2 shows the list of analytes quantified and the acronyms used in the text of this report.

Table 2. Analyte List

Compound	Acronym
2,6-Dinitrotoluene	2,6-DNT
2,4-Dinitrotoluene	2,4-DNT
1,3-Dinitrobenzene	1,3-DNB
2,4,6-Trinitrotoluene	TNT
2,4,6-Trinitrobenzene	TNB
4-Amino-2,6-Dinitrotoluene	4A-DNT
2-Amino-2,4-Dinitrotoluene	2A-DNT
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
Tetryl	Tetryl

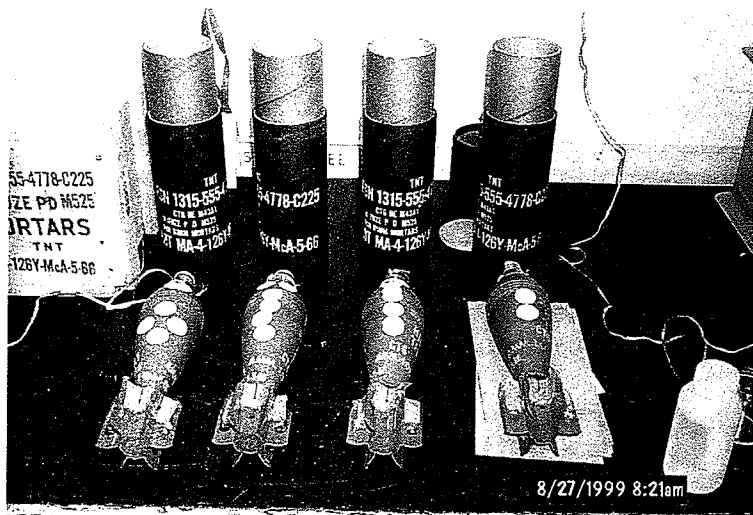


Figure 1. 81 mm Mortar Swipe Samples



Figure 2. 60 mm Mortar Swipe Samples

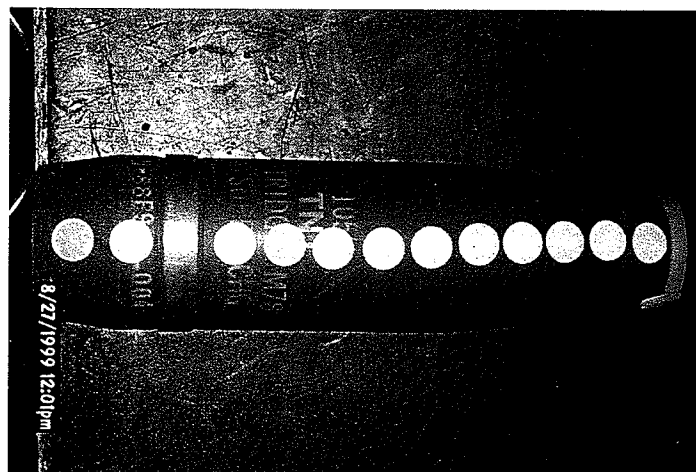


Figure 3. 105 mm Artillery Swipe Samples

Paint Scraping Tests

Paint was scraped from the nose area on mortars numbered 81-10, 60-6 and artillery 105-6. The area sampled was about 6 cm² by scraping with a knife blade. Paint scrapings were collected on aluminum foil then placed into a glass sample vial. The paint scrapings were extracted with about 3 mL of acetonitrile for one hour.

2.1.2 Results and Discussion

Surface Swipe Tests

Table 3 shows the estimated total area and the percentage of the total area sampled for each type of ordnance.

Table 3. Estimated Ordnance Surface Area and Area Sampled

Ordnance Item	Total Area (cm ²)	Area Sampled (% of Total)
60 mm Mortar	287	10
81 mm Mortar	379	8
105 mm Artillery	1277	5

Figure 4 shows a comparison of the HE filled rounds versus the TP rounds for each ordnance type. The sample values were scaled up to estimate the total mass per unit. The error bars represent one standard deviation.

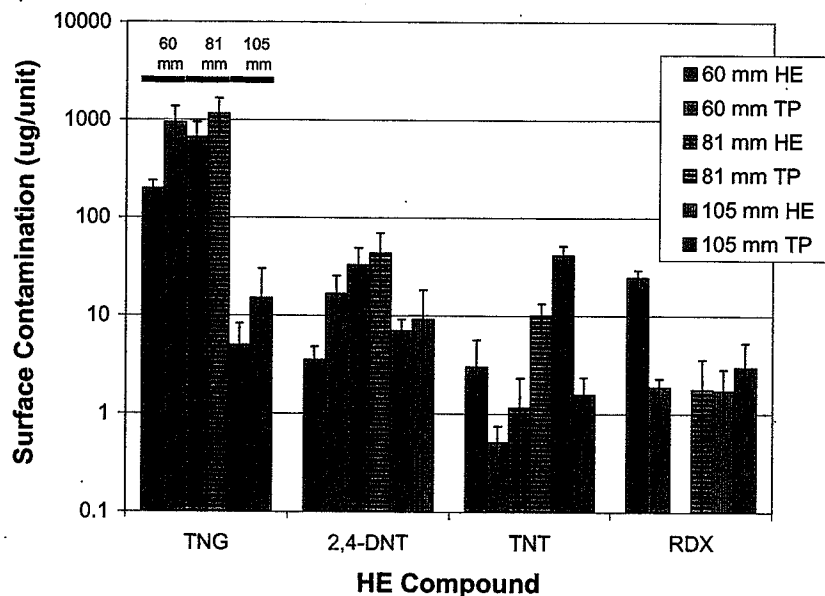


Figure 4. Methanol Removable Surface Contamination for HE and TP Ordnance

The results shown in Figure 4 show an inconsistent trend of HE versus TP surface residues. The mortars contained very high levels of trinitroglycerine (TNG) as this material is used in the propelling charge clipped to the fins on both the HE and TP rounds. During storage in the cardboard tubes, vapors emanating from the propelling charge may deposit on the surface of the ordnance. Since the 105 mm artillery is not exposed to the TNG propelling charge in storage, these levels are significantly less.

However, the presence of TNG on the 105 mm artillery may be due to contamination introduced during manufacturing, handling or storage.

For DNT, the 60 mm mortars show significantly higher levels on the TP rounds. For the 81 mm mortar and 105 mm artillery, the TP ordnance contains slightly higher, but statistically insignificant, amounts of DNT compared to the HE ordnance. For TNT, the 60 mm mortars show greater surface residues on the HE rounds (but not statistically significant). The 81 mm mortars show slightly higher amounts of TNT on the TP rounds. The 105 mm artillery shows significantly less TNT on the TP rounds.

The 60 mm mortars contained Comp B as the main charge explosive. Comp B contains 60% RDX/40% TNT. Detection of RDX for the 60 mm mortars is plausible, however, detection of RDX on the 81 mm mortar and 105 mm artillery was unexpected and may also be a result of manufacturing, handling or storage. The lower limit of detection for this method for all compounds is 0.1 to 0.3 ug/mortar or artillery. The average surface contamination was well above the detection limit for each of the compounds shown in Figure 4.

In December 1999, we were notified of an ordnance accident at Ft. Wingate, NM. This involved drilling into a 105 mm TP artillery that caused deflagration and injury to the employees. The lot numbers of the Ft. Wingate 105 mm artillery TP rounds were the same as the ones delivered to Sandia and used in the tests noted above. It is believed that this lot of 105 mm TP artillery previously contained HE and had been through a washout process to remove the main charge explosive. This process also involves repainting the unit blue to indicate a TP round.

The TNT surface contamination results for the 105 mm artillery TP show significantly less residue than the HE rounds sampled. While the Ft. Wingate accident indicates that at least one round potentially contained sufficient HE residue on the interior for a deflagration; a comparison of the TNT surface residues indicates that there was significantly less exterior surface residue on the TP rounds.

Paint Scraping Tests

Figure 5 shows the results of the paint scrape tests on the HE containing ordnance.

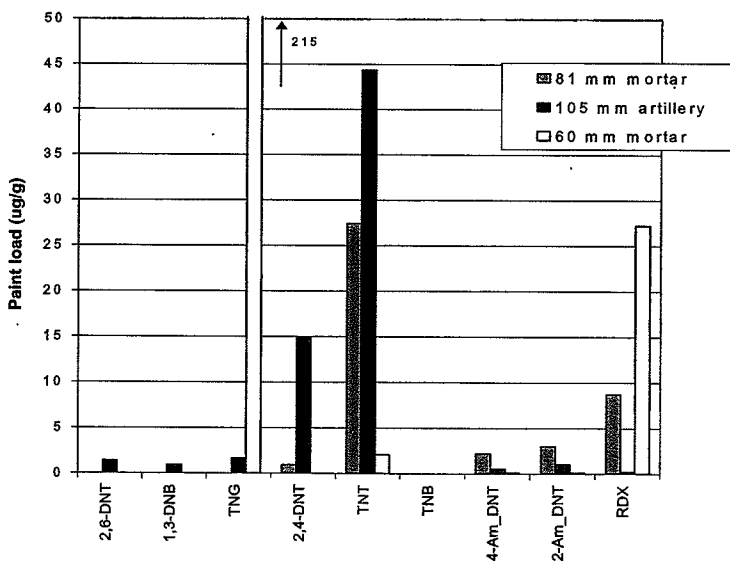


Figure 5. Paint Extract from One Sample Each of an 81 and 60 mm Mortar and one 105 mm Artillery

For the 81 mm mortar, TNG was inadvertently not quantified. There is some consistency with the surface swipe data showing

- the 105 mm HE has significant TNT in both paint and swipe data,
- the 60 mm HE mortar has high TNG and RDX in both the paint and swipe data, and
- and the 105 mm artillery HE has low TNG in the paint and swipe data.

From this limited set of surface residue testing, the results indicate that discrimination of HE from TP rounds would be difficult. For some chemical constituents the TP rounds had similar or greater surface residues, and on others the situation was reversed.

2.2 Immersion Flux Tests

2.2.1 Materials and Methods

Immersion test apparatus was constructed of stainless steel pipe welded to a flat base plate with a flat plate removable cover. A perforated plate with aircraft cable loop was used to lift the ordnance out of the immersion tube and provide a mixing mechanism. The immersion tubes were cleaned with 10% nitric acid for three days followed by a triple rinse. Figure 6 shows a picture of the immersion test apparatus for a 60 mm mortar.

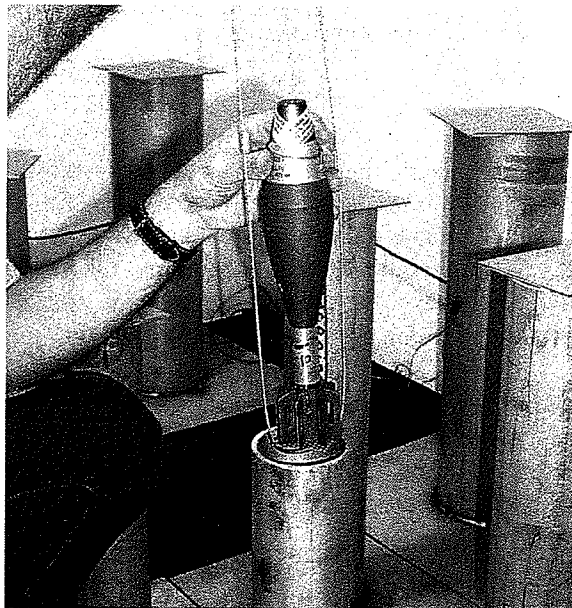


Figure 6. Immersion Test Apparatus

Two ordnance items of each type were selected for the pre-shot immersion flux tests. For the mortars, the propelling charge and initiator train was removed. The fuzes and safety wires remained in place. For the 105 mm artillery, the supplemental charge was removed and the plastic cap replaced to limit water filling the supplemental charge well. No fuze was present. The ordnance was placed in the tube and filled with deionized water – over the top of the fuze on the mortars and up to the top of the 105 mm artillery, but not allowing water to pass into the supplemental charge well. The volume of water used was 1670 mL, 2600 mL and 4540 mL for the 60 mm mortars, 81 mm mortars and 105 mm artillery, respectively. A negative control (only deionized water) and a positive control containing all analytes at 10 µg/L were prepared, complete with the ordnance lifting/mixing cable and plate. The controls contained 2000 mL of water.

Prior to sample collection, the ordnance items and the control solutions were lifted three (3) times in the immersion tubes to provide mixing. Water samples were collected with a 60 mL disposable syringe in two 50 mL aliquots (total of 100 mL) and placed into an amber glass jar. After each sample was obtained, 100 mL of deionized water was replaced into each immersion tube to keep the water at the same level. Data were corrected for dilution.

A short-term flux test was started where the ordnance was left in the water bath for 6 days with samples obtained on day 1, 3 and 6. The ordnance was then removed, water solution drained, and the immersion tube rinsed 3 times with deionized water. Then the ordnance was replaced into the immersion tube and refilled with water. This was performed because it was believed that the initial flux from the ordnance would be high due to the surface contamination. However, the longer-term flux data was sought for analysis on this project. The control solutions were not changed. For the long-term flux tests the ordnance was sampled on day 2, 11, 22, 30, 36, 43 and 65.

Analytes in the water samples were extracted using a solid phase extraction method using commercially available Porapak RDX sep-pak cartridges. Water samples are passed through a cartridge containing a divinylbenzene/ vinylpyrrolidone copolymer. Analytes are sorbed onto the solid phase media and are extracted with acetonitrile. The extract is quantified with a 1 μ L injection into a HP 6890 Gas Chromatograph equipped with a micro electron capture detector using a RTX 225 0.53mm x 6 m 0.1 μ m film thickness column. The split/splitless injector was programmed for a 220°C inlet temperature, starting column temperature of 100°C for 2 minutes, ramped to 200°C at 10°C/min, then held for 7 minutes. The splitter opened 45 seconds after sample injection.

2.2.2 Results and Discussion

Figure 7 shows the data for the positive controls. Of note are the steep to moderate declines of TNT, DNB and DNT which are compounds believed to be important to chemical sensing of buried UXO and landmines (Murrmann et al., 1971). The loss of these compounds in the water solutions introduces challenges when interpreting the flux data from the ordnance items. Charts describing the ordnance is shown as collected and not corrected for loss over time in the positive control solutions. There were no significant explosive constituents found in the negative control solutions.

Figures 8 and 9 show the results from the short-term flux tests for the 105 mm artillery showing sharp declines in the TNT and small increases in the DNT. For the 60 and 81 mm mortars, all of the analytes were at or below the method detection limits. The results from these short term tests showed that there was not a large initial release of chemical compounds from the ordnance.

The initial magnitude of ordnance 105-1 (Figure 8) was about one-third that of ordnance 105-11 (Figure 9). Review of the surface swipe data indicated that the methanol removable surface contamination were very similar (56 μ g on 105-1 and 41 μ g on 105-11). This shows that the surface swipe data are unlikely to provide good estimates of the initial chemical transfer to aqueous solutions.

Figure 10 and 11 shows the results for the long-term flux tests on the 105 mm artillery over time. This chart indicates that the principal compound of interest, DNT, continued to be emitted from the surface over a 65 day period. The estimated flux value at the end of the measurement period is about 1.25 μ g/day (based on artillery 105-11). There is no explanation for the sharp decline in TNT and DNT concentrations at about 42 days.

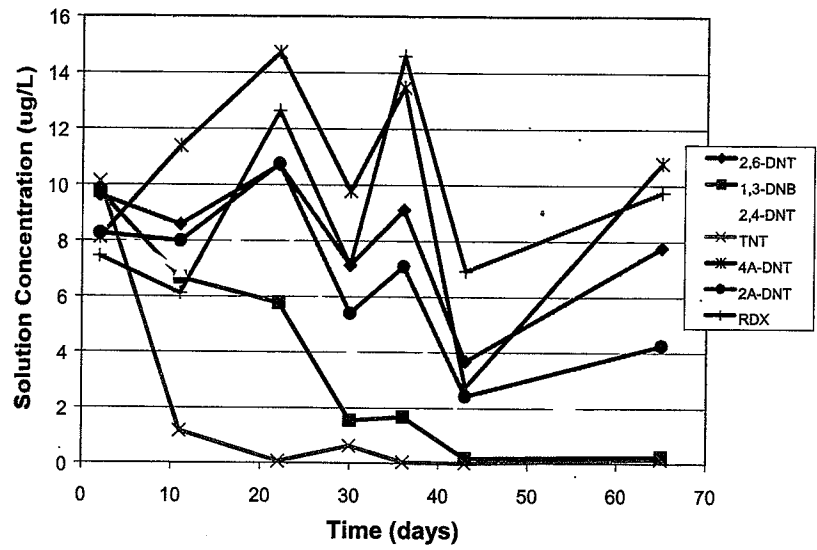


Figure 7. Positive Control (full list)

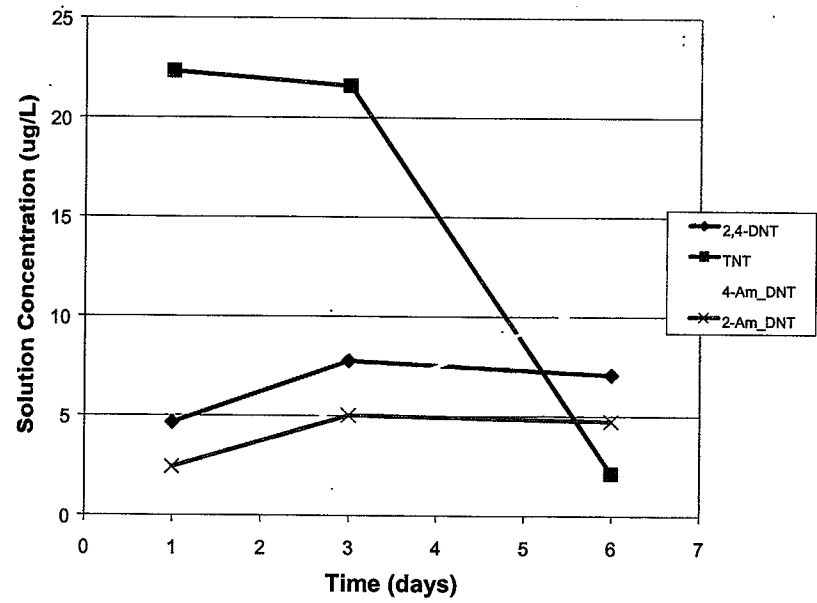


Figure 8. Short-Term Flux Test - 105 mm Artillery (number 1)

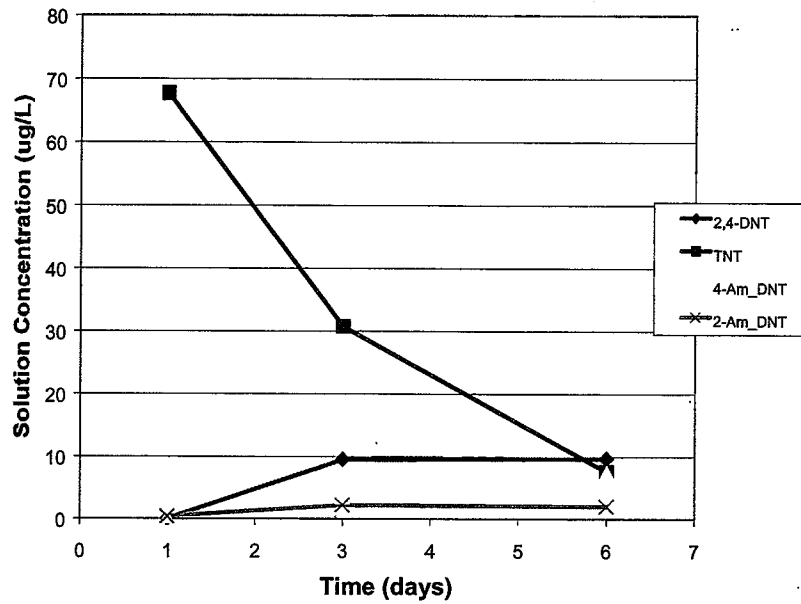


Figure 9. Short-Term Flux Test - 105 mm Artillery (number 11)

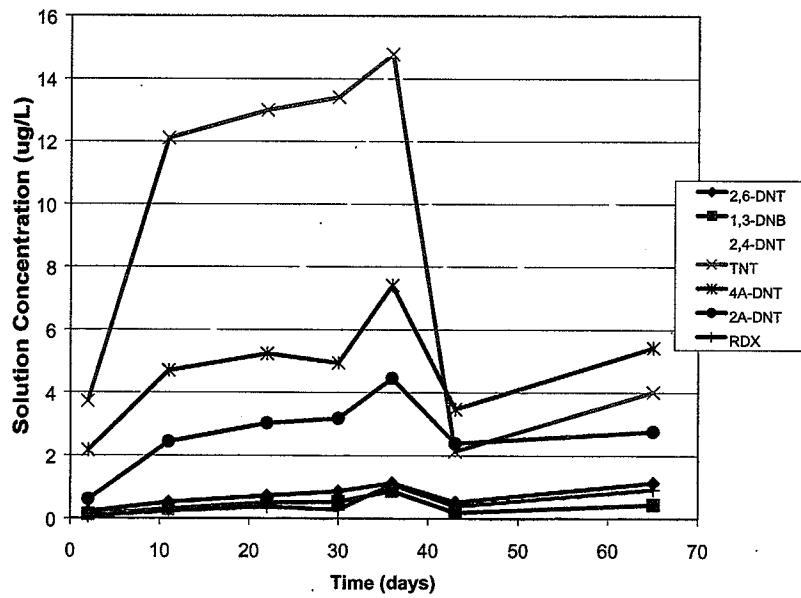


Figure 10. Long-Term Flux Test - 105 mm Artillery (number 1)

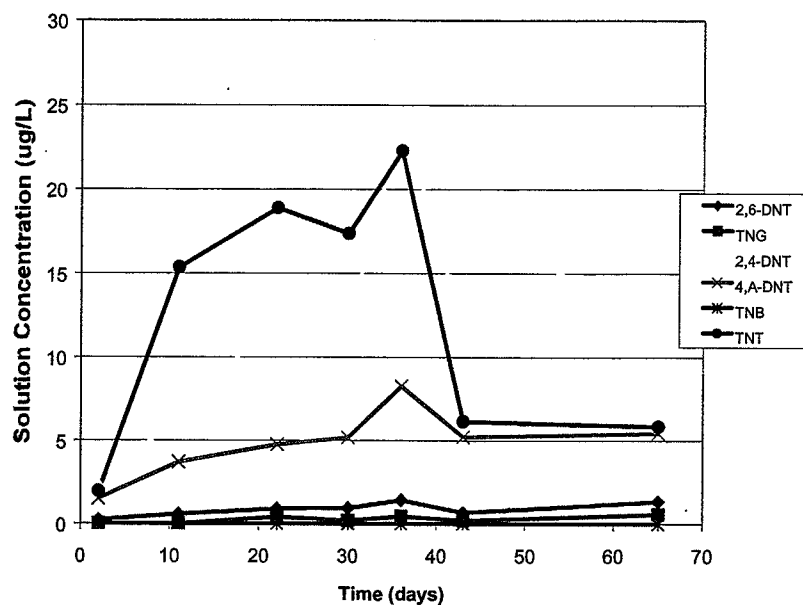


Figure 11. Long-Term Flux Test - 105 mm Artillery (number 11)

Figure 12 shows the long-term flux values for the 81 mm mortars. There was no significant flux for any of the compounds except for TNG, which is consistent with the high TNG surface residue data. Figure 13 shows the long-term flux values for the 60 mm mortars. There were no significant flux values for any of the compounds except for RDX. The 60 mm mortars are filled with Comp B, which contains RDX. It is unknown why there was not a similar trend for TNG as with the 81 mm mortars.

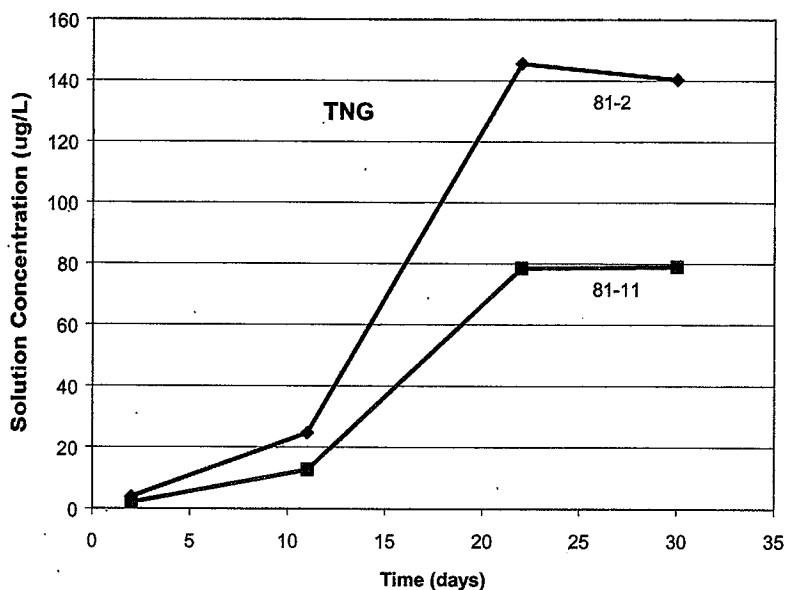


Figure 12. Long-Term Flux Test - 81 mm Mortars (number 2 and 11)

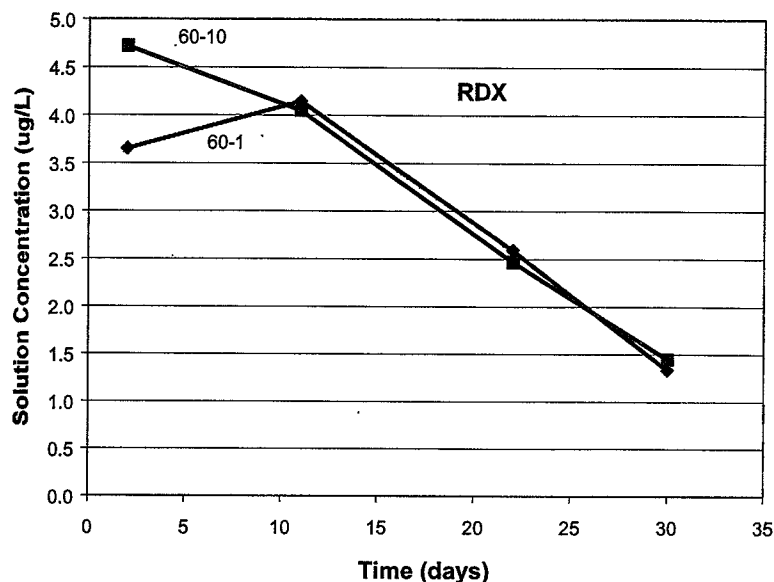


Figure 13. Long-Term Flux Test – 60 mm Mortars

The long-term tests with both the 60 and 81 mm mortars were terminated early, as a significant amount of iron oxide (e.g. rust) was observed in suspension in the water. The mortar fuse safety wires appeared to be the source of most of the rust and concern over safety led to removal of the mortars from the immersion tubes. It is believed that the suspension of rust could have sorbed or acted as a catalyst for degradation of the explosive constituents.

The pattern of chemical release into water in these pre-shot tests was inconsistent among the ordnance tested. The 105 mm artillery showed a general increase in chemical concentration for all analytes over the test period. However, for the mortars there were fewer analytes and all were at or near the analytical method detection limit. This was most likely due to the accelerated degradation of the analytes in the immersion test solution from the suspension of iron oxides derived from the safety pin wires. Degradation of these analytes in soils is a complicated process; however, the degradation rates observed here are not inconsistent with the moderate to fast degradation rates observed by others (Grant et. al, 1993 and 1995; Maskarinec et al., 1991).

3.0 Ordnance Firing and Recovery

3.1 Mortars

The mortars were fired at Sandia National Laboratories by the Marine Corps Programs Department, Fallbrook, California during the week of April 3, 2000. Explosive Ordnance Disposal technicians removed the primary explosives from all twelve of the 60 and 81 mm mortar fuses using specialized equipment.

The mortars were transported to Technical Area III and fired to the South. Figures 14 and 15 show the firing position and target location, respectively. To improve the chances of locating mortars downrange, only one propelling charge was used on each mortar. Target distance was set for about 400 to 800 meters. Figure 16 shows the impact depth of an 81 mm mortar. The 60 mm mortars were similar, or with slightly more penetration. The impact area soil is a sandy loam with few stones.

Figure 17 and 18 show the impact damage to the mortars. The paint was slightly burned and the fuse cap was slightly dented. The immersion tests were initiated the following day.



Figure 14. Mortar Firing Position



Figure 15. Mortar Target Location

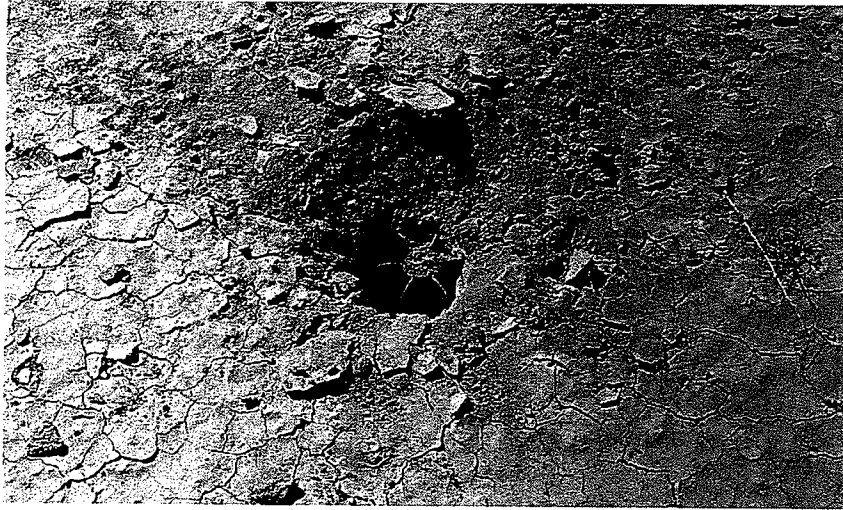


Figure 16. 81 mm Mortar Impact



Figure 17. Recovered 81 mm Mortars



Figure 18. Recovered 60 mm Mortars

3.2 Artillery

A Sandia National Laboratories owned mobile howitzer was used for the 105 mm artillery shots. To make retrieval practical, a 15 degree slope ramp was cut into the soil exposing a vertical face about 8 feet high. The mobile howitzer was placed on the ramp about 18 feet from the face of the excavation (Figure 19).

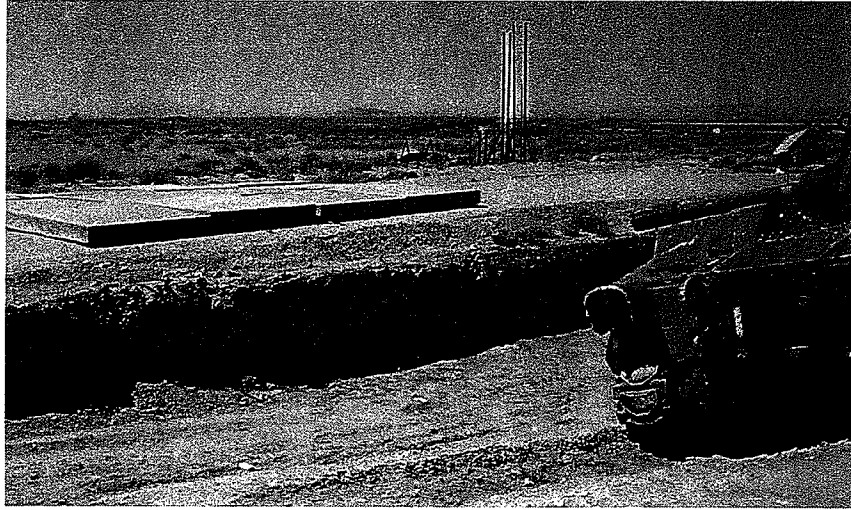


Figure 19. Mobile Howitzer and Target Location for 105 mm Artillery

Soil penetration tables (Army, 1965) were used to estimate the path length of the 105 artillery shell in this configuration. These tables indicated a trajectory length of about 10 to 20 feet. However, the trajectory path is noted to be straight for two-thirds of the length and then curve near the end. Large concrete slabs were placed on the surface about 8 feet back from the face of the excavation as a safety precaution in case the artillery trajectory turned to the surface.

Figure 20 shows the ejected soil from a target practice round shot on April 7, 2000.



Figure 20. Target Practice Round Shot

Figure 21 shows the impact crater from the first shot. Two target practice rounds were fired before recovery action began.

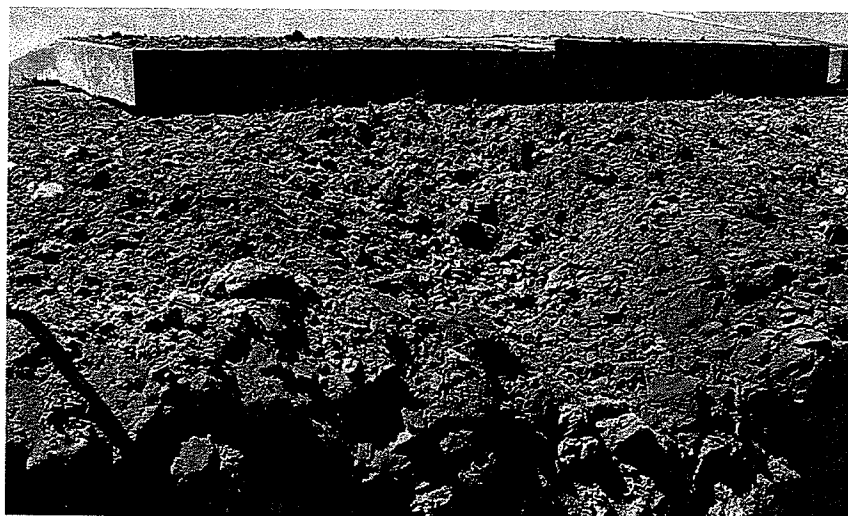


Figure 21. Target Practice Round Impact Location

Figure 22 shows the recovered target practice rounds. The nose cones broke free from the body on both of the rounds. Figure 23 shows the excavation needed to locate these items. Both items were located about 7-8 feet in from the face of the excavation and about 4 feet below the surface. These are less than the soil penetration table estimates due likely to nose cone damage making penetration more like a blunt nose shape.



Figure 22. Recovered Target Practice Rounds



Figure 23. Target Practice Round Recovery Excavation

On April 8, 2000, the 105 mm artillery HE rounds were fired. An inert fuse was attached to each round and fired with a full bag of propellant. Figure 24 shows a picture of the debris cloud from this shot. The soil ejected from this shot was much greater than for the target practice round. Two rounds were fired prior to recovery actions. Recovery action found that both of these shots resulted in low order detonation of the artillery. Figure 25 shows evidence of neat HE main charge remaining on the interior of a piece of fragment. Figure 26 shows the number of pieces recovered from both low order detonations. There was a large number of soil aggregates containing black soot residue. This black residue was scraped from the soil surface, extracted 5:1 with acetonitrile and analyzed by GC/ECD for explosive constituents. Table 4 shows the results, which indicate very high levels of explosive residues.

Table 4. Explosive Residues from Soot on Soil (Figure 27) ng/g

2,6-DNT	2,4-DNT	DNB	TNT
420	4,040	300	1,382,500
TNB	4A-DNT	2A-DNT	RDX
3,600	970	1,670	not detected



Figure 24. HE 105mm Artillery – Low Order Detonation

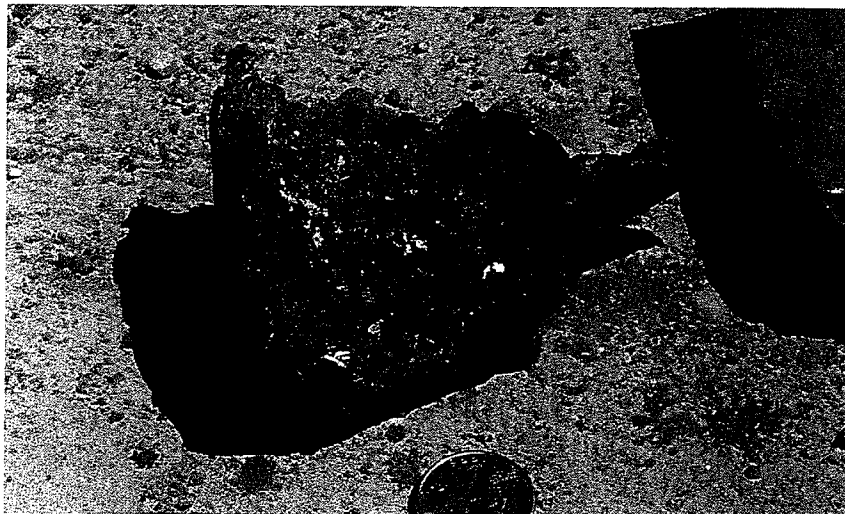


Figure 25. HE Residue on Frag from Low Order Detonation

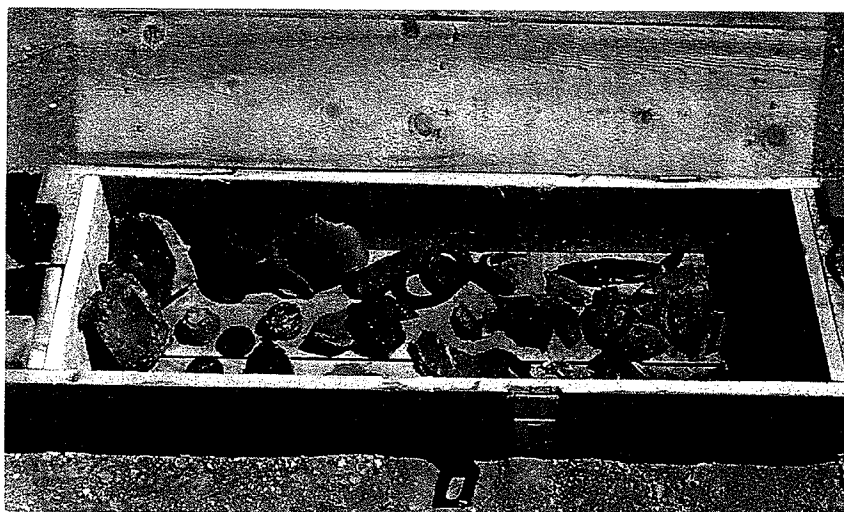


Figure 26. Debris from Two Low Order Detonations

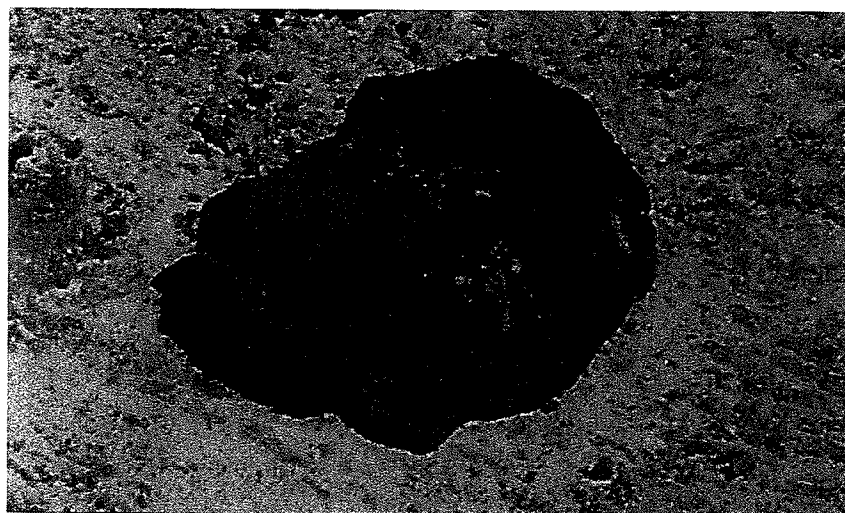


Figure 27. Low Order Detonation Residue on Soil Aggregate

A low order detonation was not desired for these shots. Analysis of the events indicated that the muzzle velocity of the artillery needed to be significantly reduced. These first shots used a full single bag of propellant as provided. An alternative propellant bag one-third the size was used in the next test on May 20, 2000. Figure 28 shows yet another low order detonation. Figure 29 shows a fragment containing a large amount of undetonated TNT. There were two such large pieces; the second was the entire bottom quarter of the round.



Figure 28. Low Order Detonation (1/3 bag propellant)

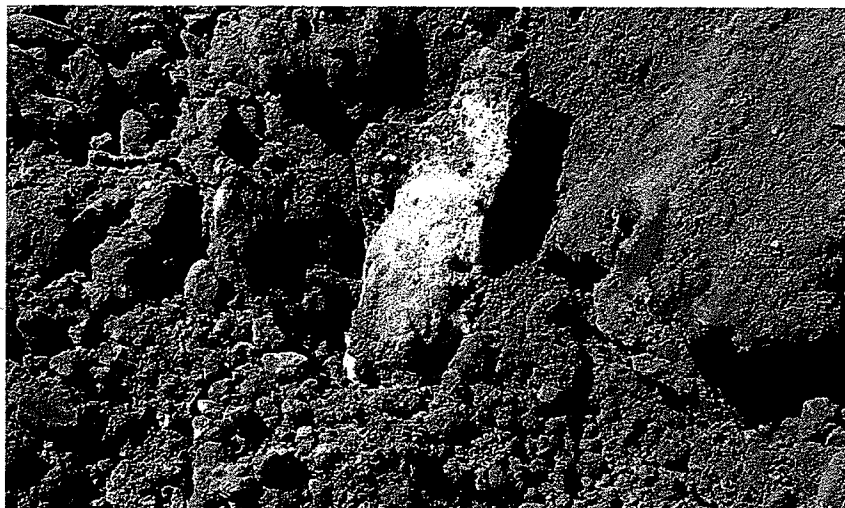


Figure 29. Low Order Detonation Debris (1/3 bag propellant)

To reduce the muzzle velocity even further, a one-third bag of propellant was separated in half producing a one-sixth bag. Figure 30 shows that this muzzle velocity was sufficiently low to prevent a low order detonation.

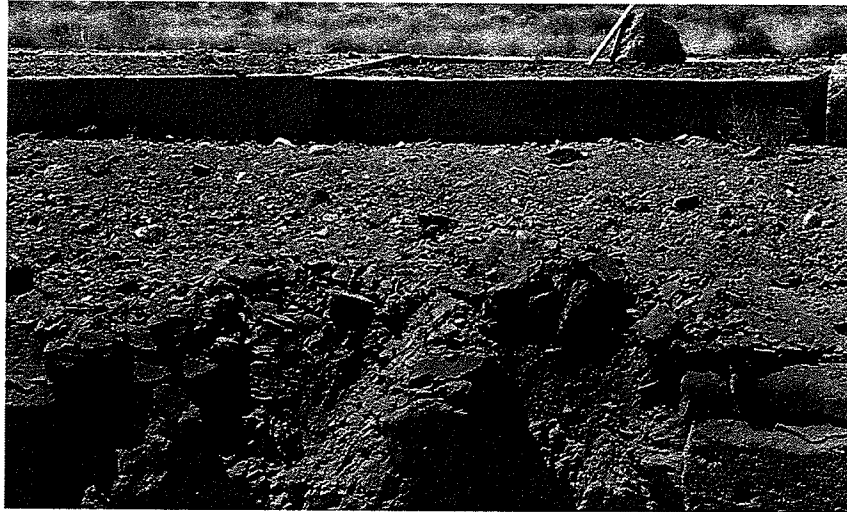


Figure 30. Successful Impacts (2) without Detonation (1/6 bag propellant)

Three each 105 mm HE artillery were fired before recovery action proceeded. The approximate depth and angle of penetration was identified by placing a PVC pipe into the penetration hole. Excavation was performed with a backhoe. A metal detector was used to search in the excavation to locate the round. Final excavation was completed by hand. The trajectory was straight for about 8 feet followed by either a curving down (2 each) and a curving up (1 each). Estimated total distance that each artillery round traveled was about 12 feet. Figure 31 shows one of the curve down rounds in place prior to recovery. Figure 32 shows a visual inspection of each round. One of the fuses broke from the round during the trajectory.

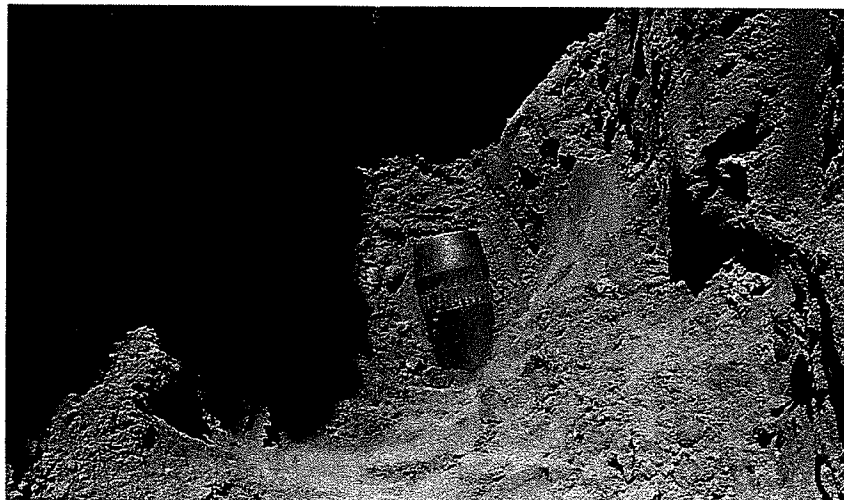


Figure 31. Recovery of 105mm Artillery



Figure 32. Visual of Each 105mm after Recovery

After recovery, each round was placed back into the cardboard shipping container for transportation to the immersion test facility.

4.0 Post-Firing Chemical Signatures

4.1 Removable Surface Contamination

The surface swipe tests were completed about 24 hours after recovery of the mortars. Figure 33 shows a comparison of the detectable surface residues before the shots and after recovery. The TNG and the 2,4-DNT levels declined significantly for both mortar types. The TNT and RDX both seemed about the same at levels about ten times the detection limit.

For the 105 mm artillery shells, there was a delay of four months before the surface swipe tests were performed. In this time, the recovered 105 mm artillery remained in the original shipping tube located in a storage magazine. It is uncertain what effect this might have had on the surface residue, however, the change from pre-shot conditions appeared minimal.

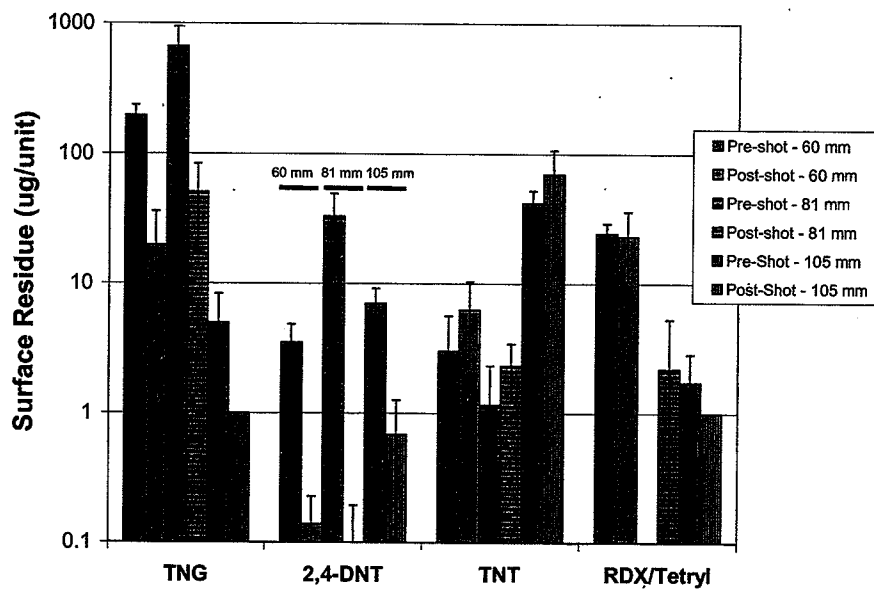


Figure 33. Comparison of pre- and post-shot swipe tests

4.2 Immersion Flux Tests

The immersion tests were started after completion of the surface swipe tests. Figure 34 shows the positive control changes over time. As with the pre-test case, loss of all analytes occurred, indicating some biochemical degradation or volatilization. The RDX and Tetryl co-eluted in the chromatography and hence start at twice the value of the other compounds.

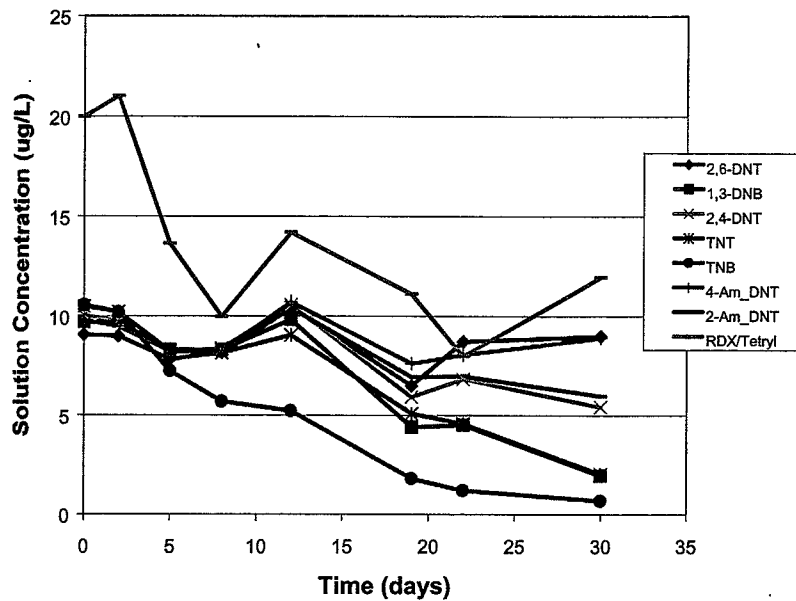


Figure 34. Positive Controls for Mortar Tests

For both the 60 and 81 mm mortars, the average solution concentration declined over the duration of the immersion test (Figures 35 and 36). These both follow the same trend as the positive controls, indicating that any leaching from the ordnance must be less than the biochemical degradation occurring in the test apparatus. Detection limit for this sampling and analysis system is about 0.25 $\mu\text{g/L}$.

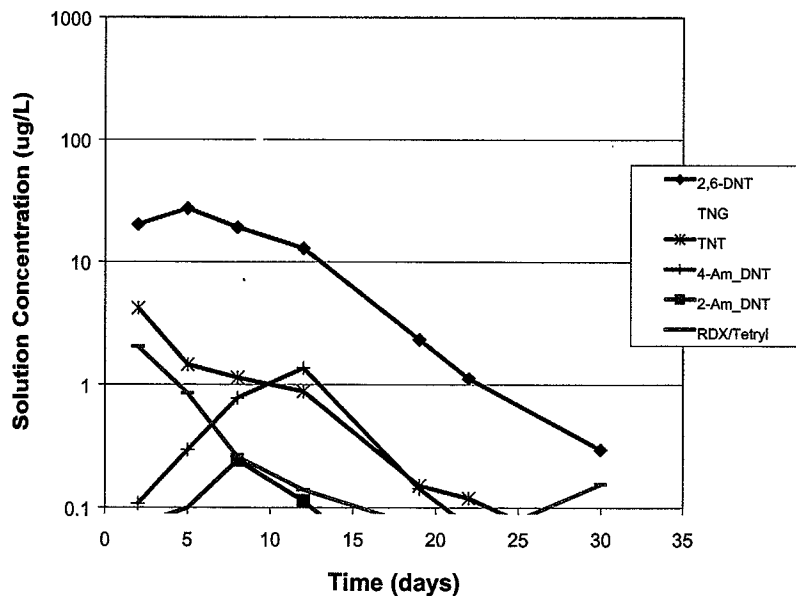


Figure 35. 81 mm Post Shot Immersion Test Results

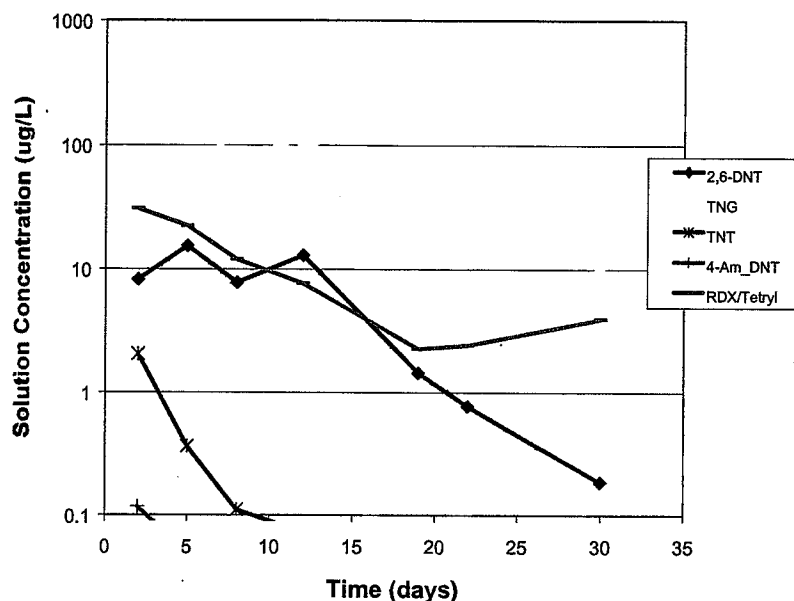


Figure 36. 60 mm Mortar Post-Shot Immersion Test Results

For the 105 mm artillery, the post-firing immersion tests were begun after the surface swipe tests were completed. For two of the three rounds, the fuses were still intact and remained as recovered. One fuse broke off on impact (see Figure 32). The immersion test for this item was completed with the water level high enough to fill the supplemental charge well located below the fuse. Figure 37 shows the positive control (established at 5 $\mu\text{g/L}$) with similar variability and decline as for the mortar post-shot positive controls.

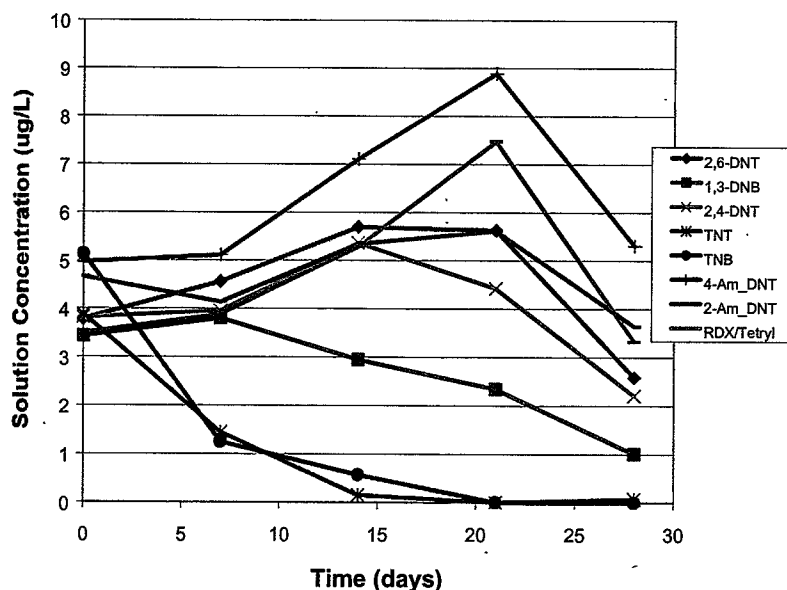


Figure 37. 105 mm Artillery Post-Shot Positive Controls

Figure 38 shows the post-shot 105 mm artillery immersion test results. These have similar patterns of loss over time as the mortars. The three post shot 105 mm artillery shells contained

very different initial concentrations of TNT. One started at 1200 µg/L, one at 250 µg/L and one was below the detection limit. The highest one was also the unit without the fuse. Expected concentrations based on the surface swipe data would be around 15 µg/L (similar to the pre-shot immersion test values, Figures 10 and 11). One potential explanation for the high case is a result of transfer of surface contamination from the interior surface of the supplemental charge well.

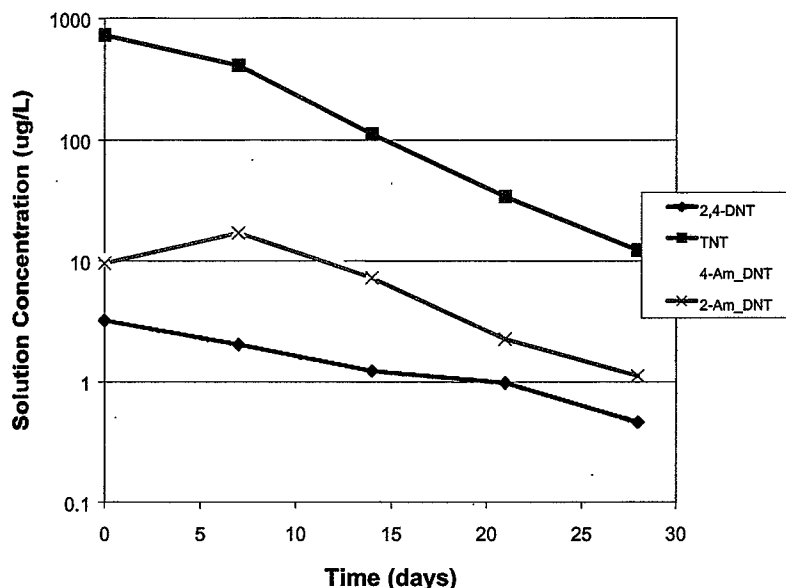


Figure 38. 105 mm Artillery Post-Shot Immersion Test Results

The pattern of post-shot immersion test data is indicative of an initial transfer to the test solution followed by degradation and loss over time. This is very different compared to the 105 mm artillery pre-shot immersion tests that showed a net positive flux to the test solution over time. No direct comparison can be made with the pre-shot mortar data as that test was compromised by the formation of an iron suspension that induced analyte degradation. From the post-shot immersion test data, one can interpret that mass transfer of chemical constituents from the UXO is significantly less than the degradation rate in the test apparatus. One may then conclude from this limited data set that chemical sensing of UXO may be unsuccessful due to the low chemical leakage rate and the high degradation rate.

5.0 UXO Field Site Characterization

5.1 Southwest Proving Ground

Through the Army Corps of Engineers, Huntsville, contacts were made available to coordinate the collection of soil samples from the Formerly Used Defense Site (FUDS) located at Southwest Proving Ground (SWPG) in Hope, AR. The purpose of this effort was to quantify the explosive chemical residue adjacent to shallow buried UXO that had been in place for a long period of time. Soil residues would document the combined effect of UXO leakage and environmental distribution and degradation.

This site was last used in 1946 at the end of WWII. Our objectives were to obtain 75% of the samples from live HE containing UXO and 25% of the samples from inert UXO from each ordnance type (e.g. 155 mm, 105 mm, 90 mm, 75 mm,, 60 mm). An equal number of ordnance types were not expected to be found. Our goal was to end up with soil samples from five (5) live HE containing UXO of each type. Classification (live vs. inert) of the UXO was completed upon detonation, which occurred subsequent to collection of the soil samples. We traveled to SWPG in early November 1999.

The operations at the site were pre-planned for comparison of mag/flag and electromagnetic induction. Anomalies were located using mag/flag and visual means. Intrusive identification of the magnetic anomaly was performed by hand with shovels. When ordnance was located, soil samples were collected adjacent to the item. A plastic hand trowel was used to completely fill a four (4) ounce wide mouth clear glass jar at each sample location. Five (5) individual soil samples were collected, equidistant, in a line from the tip to the tail. Samples were as close as possible and beneath the UXO item. Figure 39 shows the large number of magnetic anomalies (flags) and the magnetic anomaly detector (Shonstad) at the site.



Figure 39. Southwest Proving Ground Mag/Flag Anomalies

Table 5 shows the number of HE and TP items sampled. Figure 40 shows an example of one of the 155 unfused artillery lying just below the ground surface.

Table 5. Summary of UXO Sampled at SWPG

	HE		TP	
	Fused	Unfused	Fused	Unfused
155 mm	1		6	1
105 mm	5		1	
81 mm	7	1		
75 mm	4		1	1
60 mm				1
Background - 5 locations				

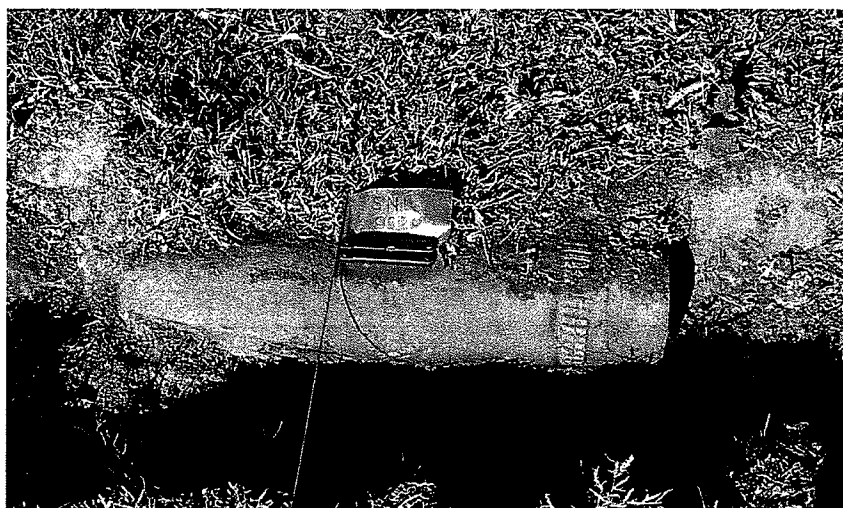


Figure 40. 155 mm Unfused Artillery at Southwest Proving Ground

Table 6 shows the analytical results from each of the samples collected at SWPG. These results do not show a discernable pattern that would allow discrimination of HE versus TP items. The 95% confidence interval method detection limit is about 5 – 10 ng/g for all the analytes and the majority of the detectable results in this range. With values at the method detection limit, there is much more uncertainty that these values are actually greater than zero. There are several factors that may have contributed to the limited residues found in these samples. The length of time since the last shot was fired was about 56 years ago. The data from the swipe and immersion tests shown above indicate that ordnance items that are fairly intact have little to no chemical release after the initial surface deposits are released. Weather cycles at SWPG include very warm and wet periods that will enhance the biodegradation of these compounds.

Table 6. Southwest Proving Ground Soil Residues (ng/g)

Sample Name	DNB	2,6-DNT	2,4-DNT	TNB	TNT	4ADNT	2ADNT	RDX
24B 0001 Background			7.3					
24B 0031 Background								
24B 0119 Background								
24B 0150 Background								
24B 0154 Background					30.5			
SNL-0001 155mm Fused								
1								
2			5.2					
3								

Sample Name	DNB	2,6-DNT	2,4-DNT	TNB	TNT	4ADNT	2ADNT	RDX
4			5.1					
5	28.3		8					
SNL-0002 155mm Unfused								
1								
2			5.1					
3			7.8					
4			7.8					
5			8.1					
24B 1339 75mm Unfused								
1			7					
2	47.8		6.8					
3								
4			6.4					
5			13					
307 81mm HE Fused								
1						43.7	14.4	
2								
3								
4					5.8			
5							5.7	
503 81 mm HE Fused								
1	28.1			9.2		6.5	8	
2								
3					5.2			
4								
5								
0026 81mm HE Unfused								
1	13.1		5.9	9.1		6.3	5.6	
2								
3								
4				10.3				
5			5.4			9.3	11.1	
155 Fused 1240								
1								
2								
3								
4								
5								
155mm 1255 fused								
1								
2								
3								
4			10.1					
5								
75mm HE Fused 0026								
1								

Sample Name	DNB	2,6-DNT	2,4-DNT	TNB	TNT	4ADNT	2ADNT	RDX
2								
3								
4								
5								
105mm HE Fused 0263								
1								
2								
3								
4								
5								
105mm Fused 0792								
1								
2								
3								
4								
5								
75 mm Fused 0066								
1								
2								
3								
4								
5								
105mm HE Fused 0318								
1								
2								
3								
4								
5								
105mm HE Fused 0730								
1						1		
2								
3								
4								
5								
75mm HE Fused.0022								
1								
2								
3								
4								
5								
81 mm HE Fused 0337								
1								
2								
3						1.1		
4								
5								
105mm HE Fused 0074								

Sample Name	DNB	2,6-DNT	2,4-DNT	TNB	TNT	4ADNT	2ADNT	RDX
1								
2								
3								
4								
5								
81mm HE Fused 2D 124								
1					6.3	2.9		
2						2.1		
3						2		
4						1.3		
5						1.6		
81mm HE Fused 4C 0073								
1					1.9	2.4	1.7	
2						1		
3								
4								
5								
60mm Unfused 4C 0255								
1			2.6		25	29.7	30.9	
2					2.6	17.1	13.3	
3						1.6	1.4	
4								
5								
81mm HE Fused 5D 0096								
1								
2								
3					1.3			
4								
5						8.6	12	
81mm HE Fused 13B 0026								
1								
2								
3								
4								
5								
155mm HE Fused 5D 0095								
1								
2								
3								
4								
5								
5D 75mm HE Fused 0086								
1								
2								
3								
4								
5								

Sample Name	DNB	2,6-DNT	2,4-DNT	TNB	TNT	4ADNT	2ADNT	RDX
5D 105mm HE Fused 00035								
1								
2								
3								
4								
5								
5D 75mm HE Fused 0028								
1								
2								
3								
4								
5								
155mm Fuzed 0646								
1					4.5			
2								
3								
4								
5								
155mm Fuzed 1171								
1								
2								
3								
4								
5								
155mm Fuzed 039								
1								
2								
3								
4								
5								

5.2 Kaho'olawe Island

The Kaho'olawe Island site was chosen for sampling as it represented a location having a climate that would preserve chemical residues that leaked from UXO. The limited rainfall and persistent dry soil condition will preserve soil residues for an extended time period. Biodegradation needs both warm and wet conditions to prevail. On August 30 and 31, 2000 seven UXO items were sampled at Kaho'olawe in a similar fashion as for Southwest Proving Ground. These items were mostly found on the surface during previous visual inspections of the site. Figures 41 through 47 shows pictures and tabulated results for each item. Figures 42, 43 and 45 show very high soil residues adjacent to UXO items with severe case corrosion. Figures 41, 44, and 47 have mostly low values under ten times the method detection limit (95% confidence interval). The UXO item in Figure 46 was a unit that contained ammonium picrate as the main charge explosive. This material is extremely soluble in water and its presence provides a historical record of the arid conditions at Kaho'olawe. Appendix A contains results from samples collected to evaluate the post-blast residue from detonation of UXO found on Kaho'olawe. Appendix B contains results from samples collected at a target site to assess the potential for residual contamination at a range target.



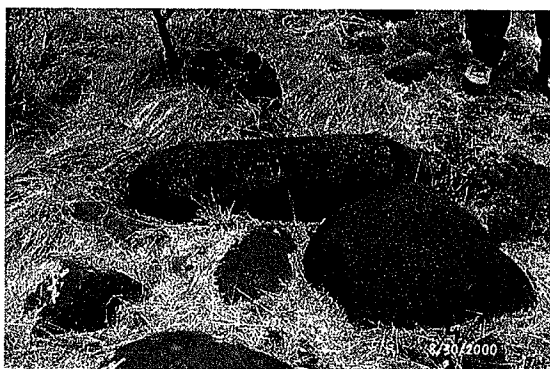
Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		3	13			
2			5			
3			6			
4 (tail)			7			

Figure 41. BIP 9205, 155 mm Projectile and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		351	691	14		
2		84	80	27	31	
3		631	877	127	176	
4 (tail)		36	20			

Figure 43. BIP 8753, 100 lb. Bomb and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		9910	894051	21565	23707	
2			4	24	12	
3		24		162	67	
4 (tail)		230	769	645	266	

Figure 42. BIP 14093, 250 lb. Bomb and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)			11			
2			5			
3			6			
4 (tail)			32			

Figure 44. BIP 14149, 5 inch Projectile and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)		9	42			
2		12	20			
3		21	27			
4 (tail)		297	586	36	49	

Figure 45. BIP 8754, 5 inch Projectile and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)			68			
2			12			
3			9			
4 (tail)			10			

Figure 47. BIP 9143, 5 inch Rocket and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (nose)						
2						
3						
4 (tail)						

* Yellow material confirmed as ammonium picrate

Figure 46. BIP 14070, 5 inch Projectile and Sample Results (ng/g)

6.0 Summary and Conclusions

Unexploded ordnance is recognized as a significant legacy related to military testing and training activities. Cleanup of active and former range sites has been challenged with the difficulty of discriminating unexploded ordnance from target practice rounds, ordnance fragments and other range scrap. The main charge energetics that remains in unexploded ordnance is a unique feature that could be exploited to distinguish these items. Trace chemical sensing of the residue emitted from unfired ordnance and unexploded ordnance has been evaluated in this work.

A small subset of ordnance items (60 and 81 mm mortars, 105 mm artillery) were selected to be representative of the type of unexploded ordnance typically found on military ranges. The chemical signature of this ordnance was evaluated by sampling the surface residue and measurement of the leakage into water during periods of immersion.

The explosive residue found on the surface of new unfired ordnance was not uniquely different from that found on target practice rounds. This may be an effect of storage and handling where cross contamination is not avoided. Pre-shot immersion test results showed a net positive flux for the 105 mm artillery; however, the mortar fuse safety wires produced a suspension of iron oxides that are believed to have caused sorption or degradation of chemical constituents in the mortar immersion tests.

Fuse primary explosives were removed and ordnance was fired with conventional means. Post-shot surface residues showed a decline in some chemical constituents and no change in others. Post-shot immersion tests showed a gradual decline in chemical constituents, which indicate that the emitted flux was less than the degradation rate.

Sampling soil adjacent to unexploded ordnance items in the field was performed at two locations: Southwest Proving Ground near Hope, AR and Kaho'olawe Island, HI. The results from SWPG showed small soil residue values, most near the method detection limit, that failed to show any distinguishing character from target practice rounds. Several of the units sampled at Kaho'olawe showed very high soil residues adjacent to severely corroded unexploded ordnance bombs. The unique arid climate at Kaho'olawe supports preservation of any emitted chemical signature, since moisture is necessary for biotic and abiotic chemical reactions.

The results of this work indicate that the chemical signature emitted from simulated unexploded ordnance is insufficient as a distinguishing character for use in discrimination of live explosive containing items. The rate of biochemical degradation processes for these chemical constituents appears to exceed the flux derived from the main charge explosive. This is supported with field soil residues collected at Southwest Proving Ground. However, in arid environments where the biochemical degradation processes are limited, accumulation of explosive chemical signatures does occur.

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Appendix A

Post-Blast Residue from UXO Demolition Activities

A.0 Post Blast Residue from UXO Demolition Activities

A.1 Introduction

While at Kaho'olawe Island, soil samples were collected in and around recent UXO demolition activities. The purpose of this effort was to assess the level of post-blast residue that might warrant further evaluation with respect to environmental contamination. Limited samples were collected only to complete a screening assessment for the types of UXO destroyed and the type of demolition activity.

All UXO demolition samples were taken on the OB/OD range. Individual UXO items were detonated by use of a shape charge, except for the old Navy demolition pit. This location was repeatedly used as a central demolition location for UXO collected from the range and deemed safe for transport. It was reported that Composition C-4 was used on groups of UXO placed into the demolition pit. Typical operations would entail three weeks of training range use, followed by one week of Explosive Ordnance Disposal team collection of UXO and demolition. No attempt was made to collect use records on the old Navy demolition pit as part of this effort.

The UXO items were destroyed about one week prior to sample collection. The time since the last use of the old Navy demolition pit was not determined.

A.2 Materials and Methods

Four soil samples were collected randomly in the crater where the UXO item was destroyed. Soils were analyzed using EPA Method 8095. This method extracts explosive residues from 0.8 g soil using 4 mL of acetonitrile in a temperature (15°C) controlled ultrasonic agitator for 18 hours. Acetonitrile extracts are filtered through a 0.45µm disposable syringe filter directly into an autosampler vial. Samples are quantified with a 1 µL injection into a HP 6890 Gas Chromatograph equipped with a micro electron capture detector and a RTX 225 0.53mm x 6 m 0.1 µm film thickness column. The split/splitless injector was programmed for a 220°C inlet temperature, starting column temperature of 100°C for 2 minutes, ramped to 200°C at 10°C/min, then held for 7 minutes. The splitter opened 45 seconds after sample injection.

A.3 Results and Discussion

Figures A1 through A9 show a picture and table of analytical results for each of the four samples collected at each site. Only six of the analytes are shown as all others were below method detection limits (about 5-10 ng/g). Samples collected from individual UXO demolition efforts generally showed very low concentrations of all analytes with one notable exception. Figure A3 shows the results from detonation of a 1000 lb semi armor piercing bomb that contained a 100 lb HE dispersing charge. The demolition produced very high levels of TNT.

The old Navy demolition pit (Figures A1 and A2) show very high levels of RDX that may be a result of the repeated use of Composition C4 in the process.



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (side)		11				7829
2 (side)						72
3 (bottom)						11634
4 (bottom)		30		50	13	354

Figure A1. Bottom of Old Navy Demolition Pit and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1 (closest)		7	14	7	13	140
2						
3		2				2260
4 (farthest)		10				85

Figure A2. Downwind of Old Navy Demolition Pit and Sample Results (ng/g)



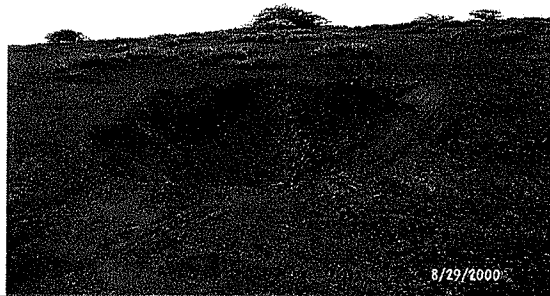
Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1			65142	2248	1750	
2			142993			
3			358040			
4			1129939			

Figure A3. BIP 9235, 1000 lb. Semi-Armor Piercing Bomb (containing 100 lb HE) and Sample Results (ng/g)

No Picture

Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1			3	3		
2	1		2	6	2	
3			1	4	2	
4			2	5	2	

Figure A4. BIP 9243, 81 mm Mortar and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1						
2						
3						
4						

Figure A5. BIP 9222, 500 lb Bomb and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1				6	6	28
2		30		3	2	
3		2	3	2	2	
4			2			22

Figure A7. BIP 9200, 250 lb Bomb and Sample Results (ng/g)



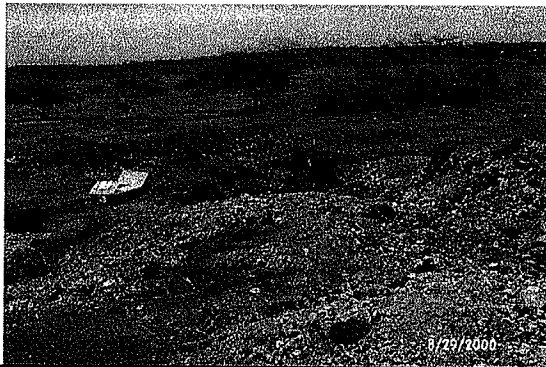
Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1			12	2		23
2			2			
3						
4			2	4	3	

Figure A6. BIP 9188, 600 lb Bomb and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1	2		4	1		
2	1		9	1		
3			9			
4	2		5	2		

Figure A8. BIP 14109, 3 Mortars and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	.4ADNT	2ADNT	RDX
1		4	3	2		
2	3		2	2		448
3			1			
4			2			

Figure A9. BIP 9202, 81 mm Mortar and Sample Results (ng/g)

Appendix B

Surface Soil Residues at a Target Site

B.0 Surface Soil Residue from a Target Site

B.1 Introduction

While at Kaho'olawe Island, samples were collected representing an old target site. Last use of the target site was at least 10 years previous. The location sampled was termed the Seagull site and contained several target locations. The surface soil at the site was mostly hard pan that was not amenable to sample collection. Surface soil was collected in low lying areas where wind erosion has caused localized accumulation and where precipitation runoff might have transported any explosive residues.

B.2 Materials and Methods

Four soil samples were collected in each area depicted in the pictures. Analytical methods were the same as described in Section A.2.

B.3 Results and Discussion

Figures B1 through B4 show pictures from the sampled locations and the analytical results. The results from this limited sampling showed that explosive residues were mostly absent indicating that there was not extensive soil contamination represented by the locations sampled.

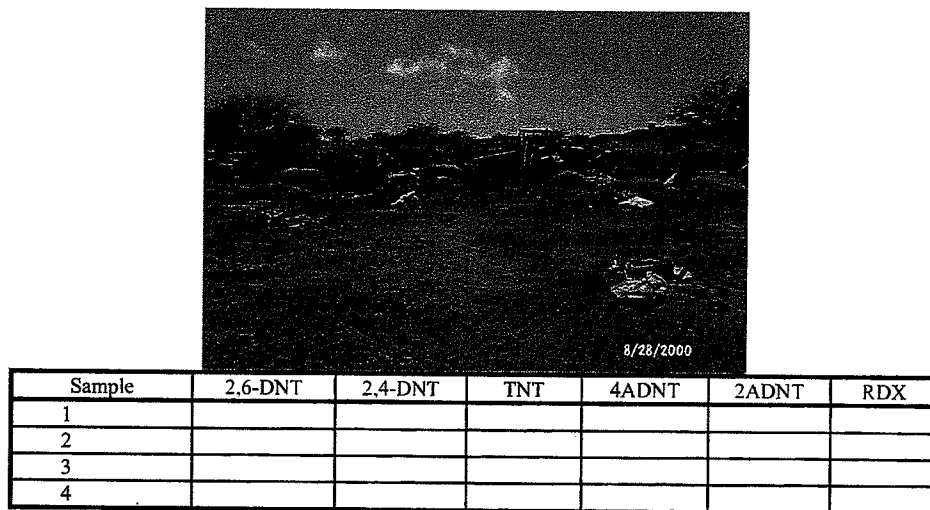


Figure B1. Seagull Target Site and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1		2	5			
2						
3						
4						

Figure B2. Seagull SAM Target Site and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1						
2						
3						
4						

Figure B3. Seagull Drainage Arroyo and Sample Results (ng/g)



Sample	2,6-DNT	2,4-DNT	TNT	4ADNT	2ADNT	RDX
1			2			
2						
3						
4						

Figure B4. Lower Seagull Area and Sample Results (ng/g)

Distribution:

1	MS0719	S.M. Howarth, 6131
10	MS0719	J.M. Phelan, 6131
1	MS0719	S.W. Webb, 6131
1	MS1452	J.A. Merson, 2552
1	MS1452	P.J. Rodacy, 2552
1	MS1452	J.L. Barnett, 2552
1	MS1425	R.J. Simonson, 1744
1	MS9018	Central Technical Files, 8945-1
2	MS0899	Technical Library, 9616
1	MS0612	Review and Approval Desk, 9612 for DOE/OSTI
1	MS0161	Patent and Licensing Office, 11500
1	Dr. Tom Jenkins U.S. Army Corps of Engineers 72 Lyme Road Hanover, NH 03755	
1	Dr. Judy Pennington U.S. Army Corps of Engineers 3909 Halls Ferry Road Vicksburg, MS 39180-6199	
2	Dr. Jeff Marqusee Strategic Environmental Research and Development Program 901 North Stuart Street, Suite 303 Arlington, VA 22203	
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5	James Putnam Pacific Division Naval Facilities Engineering Command 258 Makalapa Cr., Suite 100 Pearl Harbor, HI 96860-3134	